How different would tropospheric oxidation be over an ice-free Arctic?

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[1] Climate projections suggest that a complete Arctic sea-ice retreat is likely in the future during summer. Less ice will cause less light reflection and slower tropospheric photolysis. We use a tropospheric chemistry model to examine how oxidation may differ over an ice-free Arctic. We find that late-summer OH concentrations can decrease by 30–60% at polar latitudes, while effects on local ozone and global oxidant abundances are small. Ozone changes become larger in the more extreme case where sea-ice is also removed in spring and early summer. In this case, we find large spring ozone increases (up to 50–60%) over the Arctic, and even over inhabited high latitude regions (up to 20%), due mainly to a reduction in the impact of bromine chemistry, caused by the sea-ice retreat. Annual mean ozone also increases in the run with the summer/spring sea-ice removal, but not in the simulation including only late-summer sea-ice removal. **Citation:** Voulgarakis, A., X. Yang, and J. A. Pyle (2009), How different would tropospheric oxidation be over an ice-free Arctic?, *Geophys. Res. Lett.*, *36*, L23807, doi:10.1029/2009GL040541.

1. Introduction

[2] The Arctic is often thought of as a completely remote region, given the lack of large anthropogenic emission sources in its area. However, studies have shown that there is substantial transport of air pollution to northern polar latitudes, originating in North America and, more importantly, Eurasia [*Klonecki et al.*, 2003; *Eckhardt et al.*, 2003; *Stohl*, 2006; *Law and Stohl*, 2007; *Quinn et al.*, 2008; *Shindell et al.*, 2008]. Also, in the future, the opening of new shipping routes through the Northern passages could lead to substantial further increases of the amount of ozone precursors present in the Arctic [*Granier et al.*, 2006]. Another major characteristic of the Arctic is that it is an area which is warming faster than the rest of the globe [e.g., *Rigor et al.*, 2000], and this has started to affect the Arctic environment in many ways. In particular, there has been a significant reduction in year-round and especially summer Arctic sea-ice in recent years [*Comiso*, 2002; *Lemke et al.*, 2007] and models show that there is a large possibility for further reductions in a warmer climate [*Laxon et al.*, 2003; *Holland et al.*, 2006; *Meehl et al.*, 2007; *Wang and Overland*, 2009], with the Arctic projected to become near ice-free during summer later this century.

[3] Ground reflection of shortwave radiation can significantly modify photolysis rates in the troposphere [*Madronich*, 1987; *Laepple et al.*, 2005]. This is especially true for areas covered with snow or ice, which, as measurement studies have shown, reflect up to 90% or more of the incident radiation [*Grenfell et al.*, 1994]. Thus, the possible disappearance of the Arctic ice sheet could lead to a drastic reduction in photolysis rates, which would have a subsequent impact on local summer photochemistry. Another important feature of Arctic chemistry is the involvement of bromine species in boundary layer ozone depletion events in spring [*Simpson et al.*, 2007]. One mechanism which has been proposed as leading to these events is the sea-salt production from snow lying on sea-ice during blowing snow events and subsequent bromine release (bromine explosions) [*Yang et al.*, 2008]. In an extreme case with Arctic sea-ice removal even in spring, this process would become far less important.

[4] In this paper we use a chemical transport model (CTM) to examine the sensitivity of tropospheric oxidants to future sea-ice retreat in the Arctic. In section 2 we briefly describe the model used and the experiments performed. In section 3 we explore the impact of late-summer sea-ice removal on oxidants, principally through changes in photolysis rates. In section 4, we explore the possible effects of sea-ice removal extending through spring into summer on oxidant abundances. In this case the changes in both photolysis rates and bromine emissions are expected to be important. Finally, in section 5, the conclusions of this study are presented.

2. Model Description and Experimental Set-Up

[5] We use the Cambridge *p*-TOMCAT CTM as described by *Voulgarakis et al.* [2009a]. Detailed ozone budget calculations, which explore the radiative effect of clouds on oxidants, are described by *Voulgarakis et al.* [2009b]. The CTM accounts for 79 gaseous chemical species. The Fast-JX photolysis scheme [*Wild et al.*, 2000; *Neu et al.*, 2007] is used, with 6-hourly ECMWF cloud water content and surface albedo fields driving the radiative transfer. The simulation of tropospheric bromine chemistry follows *Yang et al.* [2005] (with sources from bromocarbons and open ocean sea-salt) and it additionally considers bromine release due to blowing snow events above sea-ice according to *Yang et al.* [2008]. Snow salinity in the Arctic is derived by extrapolating measured Antarctic salinity and monthly sea-ice coverage follows satellite observations [*Comiso*, 1990, updated 2005]. Previous studies have demonstrated that the model is generally capable of simulating lower and middle tropospheric ozone with a relatively small bias [*Voulgarakis et al.*, 2009a]. The addition of the bromine mechanism leads to reductions in ozone concentrations and to the successful simulation of bromine explosion events as seen at high latitudes from satellites. For example, our calculation of the

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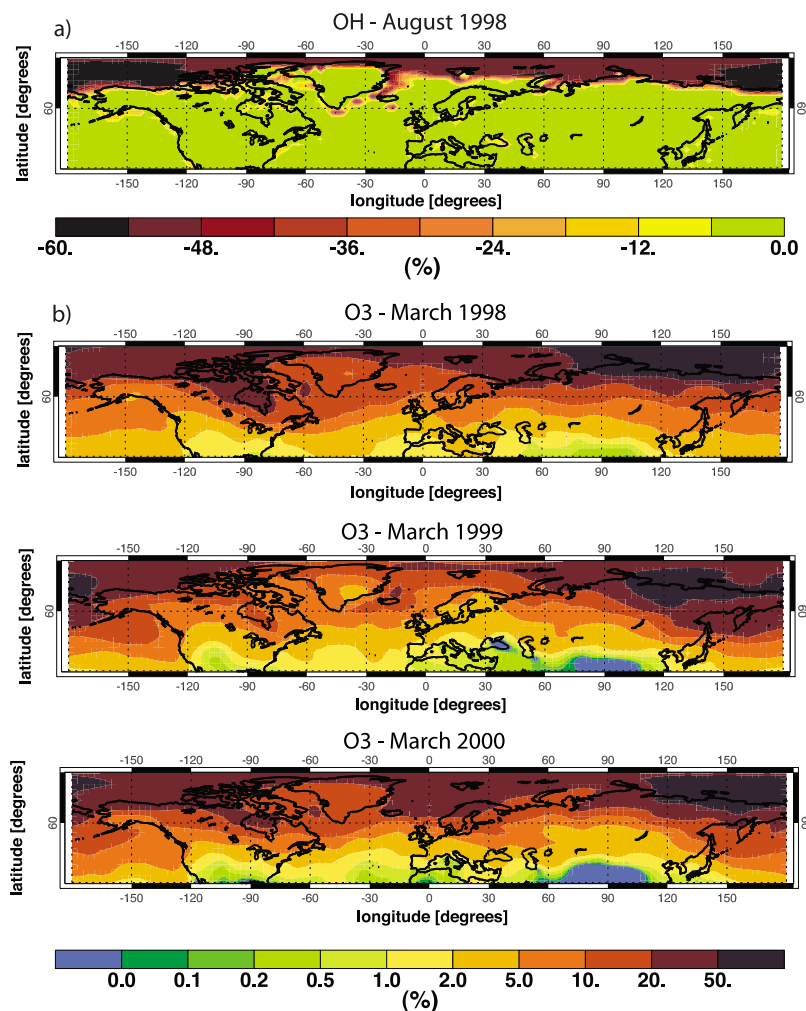
Figure 1. (a) Percentage (%) difference in monthly mean surface OH concentrations in August 1998, between the run in which late-summer sea-ice is removed (NoAugSepIce) and the run in which no perturbations were applied (BASE). (b) Percentage (%) difference in monthly mean surface ozone concentrations in March (all years), between the run in which spring and summer sea-ice is removed (NoSpSuIce) and the run in which no perturbations were applied (BASE).

present day gives boundary layer zonal daily mean concentrations of bromine oxide (BrO) around $2-3$ ppt in the high latitude spring, and an average contribution of more than 15% to boundary layer ozone destruction. For this present study, the important point is that the release of bromine depends on the presence of sea-ice; when sea-ice is removed there will be a corresponding reduction in high-latitude bromine.

[6] Four experimental runs were performed: BASE, in which no perturbation was applied; NoAugSepIce, in which sea-ice was completely removed for August–September and reduced for July and October with respect to the values in BASE; NoSpSuIce, a more extreme scenario in which Arctic sea-ice was completely removed in spring as well as in the summer; and NoSpSuIce_Alb, which was the same as NoSpSuIce except that the sea-ice perturbation was only allowed to influence chemistry through albedo effects and not through changes in the bromine chemistry. The start date of the experiments was July 1997 and the end date was December 2000, with the 6 first months being a spin-up.

The resolution we used is $2.8° \times 2.8°$ with 31 vertical layers extending up to 10 hPa.

3. Effects of Late Summer Sea-Ice Removal

[7] In this section, we examine the differences between runs NoAugSepIce and BASE, to determine how important changes in photolysis are for oxidants, following complete late-summer sea-ice retreat. Although the bromine mechanism is still included in NoAugSepIce, its effects are not expected to be important in the summer.

[8] From Figure 1a it is clear that OH concentrations are strongly impacted by the perturbation. Reductions in monthly mean surface Arctic OH during August 1998 are higher than 30%, rising locally to 60%. The geographical pattern and the magnitude of the changes show minimal interannual variability (plots for 1999 and 2000 are not shown as they are almost identical to 1998). The fact that OH is a very short-lived species explains why the changes due to sea-ice retreat are restricted only to the areas where

Table 1. Percentage Difference in Annual Mean Boundary Layer (BL) OH Concentrations, Ozone Production (P(O$_3$)), Ozone Loss (L(O$_3$)), and Ozone Burden

	NoSpSuIce-Base[a]	NoSpSuIce_Alb-Base[b]
	65°N–90°N	
BL OH	−28.0%	−21.4%
BL P(O$_3$)	−15.8%	−15.3%
BL L(O$_3$)	−37.2%	−12.9%
BL O$_3$	3.6%	−0.9%
	45°N–65°N	
BL OH	−4.0%	−2.6%
BL P(O$_3$)	−0.9%	−0.9%
BL L(O$_3$)	−4.6%	−1.5%
BL O$_3$	1.0%	−0.3%

[a]Percentage difference between the run in which spring and summer sea-ice is removed (NoSpSuIce) and the run in which no perturbations were applied (Base).

[b]Percentage difference between the run in which spring and summer sea-ice is removed with the perturbation only influencing photolysis (NoSpSuIce_Alb) and the run in which no perturbations were applied (Base).

sea-ice normally exists. We note that modelled mean OH concentrations over the Arctic in August are around $5-7 \times 10^5$ molecules/cm^3. This figure agrees with previous studies [e.g., *Spivakovsky et al.*, 2000] and underlines that the Arctic cannot be neglected as an environment for oxidation in the summer, as has also been indicated by measurement studies [e.g., *Beyersdorf et al.*, 2007].

[9] On the other hand, the effects of sea-ice disappearance on surface ozone concentrations (not shown) are small for this scenario (reductions smaller than 5% in the Arctic) but they extend to larger geographical areas, with some minimal impact found at continental regions as well. The decreases in ozone loss rates in NoAugSepIce, due to less radiation, are not so large as the decreases in its production rates, due to less OH and less peroxy radical formation, and it is the latter which drives the small ozone concentration decreases in NoAugSepIce. Note that the global effect on oxidant burden following the sea-ice removal is very small (<1% globally).

4. Effects of Summer and Spring Sea-Ice Removal

[10] Next we present a more extreme case, where sea-ice disappears not just for late summer but also for other important parts of the year for ice-oxidant interactions: spring, when bromine chemistry is very important, and early summer, when the duration and intensity of radiation in the Arctic is at its highest.

[11] In Figure 1b we show changes in surface ozone in March, caused by the retreat of Arctic sea-ice. It can be seen that there are high amplitude increases in all northern high-latitude areas, in some cases exceeding 50% in polar regions. Since ozone is a longer-lived oxidant, the positive signal is transported to lower latitudes where some inhabited areas (Northern Europe, Northern Japan, Canada) show surface ozone increases of up to 20%. In lower midlatitudes the increases range from 0 to 10%. There is some interannual variability, most likely caused by changes in the transport patterns from year to year, but the overall picture of the effects remains largely similar. For OH, there are decreases of up to a factor of 2 in March (not shown),

but they are associated with relatively small OH concentrations (due to the low amount of radiation at this time of the year). The impact of the spring OH reduction on annual OH abundances is examined in the following paragraphs.

[12] In Table 1 we show the annual mean response of the concentration of OH and ozone in the northern high and high-middle latitude boundary layer to the removal of Arctic sea-ice as simulated in runs NoSpSuIce and NoSpSuIce_Alb. Comparison of NoSpSuIce and NoSpSuIce_Alb allows us to examine the relative importance of the albedo effects and the effects on bromine chemistry on an annual scale. The effects on boundary layer OH remain large (close to 30% reduction) for this integrated case at polar latitudes. Modifications at lower latitudes are smaller but still detectable. It is noteworthy that the OH reduction is not exclusively driven by albedo changes but the decreased bromine release also plays a role. The reaction of bromine that destroys ozone (O$_3$ + Br → BrO + O$_2$) leads to BrO formation, which can then react with HO$_2$ (HO$_2$ + BrO → HOBr + O$_2$) to produce HOBr, whose photolysis produces OH. Thus bromine not only destroys ozone catalytically, but also leads to increases of the OH/HO$_2$ ratio [*Platt and Hönninger*, 2003]. Hence a reduction of bromine due to sea-ice retreat, leads to a decrease in OH. This explains the fact that runs NoSpSuIce and NoSpSuIce_Alb produce different OH concentrations, confirming that summer sea-ice removal (which affects photolysis rates but not the bromine abundance) cannot be the only reason for annual mean reduction in boundary layer OH.

[13] In Figure 2, we show the seasonal variation of OH mean concentration in the Arctic boundary layer for three different runs: Base, NoSpSuIce and NoSpSuIce_Alb. It is clear that when we remove sea-ice, OH becomes much lower for all the months of the year when radiation is substantial. However, by comparison with NoSpSuIce_Alb, we can see that in March, the entire OH reduction can be explained by the bromine effect. Also, in April, less than half of the reduction is explained by albedo effects. The fact that BrO is at its peak during those months (see dotted line on graph) enhances our confidence that bromine chemistry
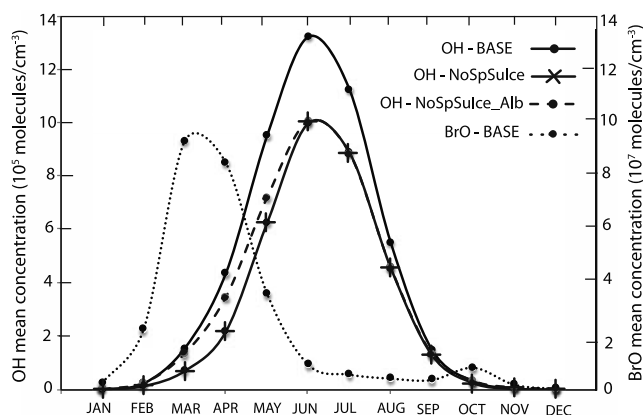

Figure 2. Seasonal variation (constructed using monthly averages from 1998 to 2000) of Arctic (65°N–90°N) boundary layer mean concentration of (a) OH in the Base run (solid line), (b) OH in the NoSpSuIce run (solid line with crosses), (c) OH in the NoSpSuIce_Alb run (dashed line), and (d) BrO in the Base run (dotted line).

drives much of this reduction, which, as was seen in Table 1, is also important for the annual mean.

[14] Note that we found a reduction in boundary layer annual mean Arctic OH of 6% (not shown) in run NoAugSepIce (only late-summer perturbation) relative to Base, which, while substantial, is much smaller than the effect of the full spring/summer perturbation (NoSpSuIce). This indicates that it is the effect of total sea-ice removal early in the summer (i.e. before August/September), when solar radiation reaches a maximum, which is responsible for the bulk of the annual mean change of Arctic OH in NoSpSuIce. On the other hand, the annual mean change of OH concentrations at midlatitudes in run NoAugSepIce is close to zero.

[15] Annual mean boundary layer ozone is 3.6% higher at polar regions when sea-ice disappears for summer/spring (NoSpSuIce). This is driven mainly by the effects on bromine release which influences ozone loss. In run NoSpSuIce_Alb, which excludes effects on bromine and only includes radiative effects of the sea-ice removal (via albedo changes in summer), the changes in $P(O_3)$ and $L(O_3)$ are comparable, thus leading to very small net effects on ozone. In NoSpSuIce, the annual effect on $L(O_3)$ (reduction of 37%) is much larger than in NoSpSuIce_Alb (reduction of 13%) because of the springtime bromine decrease in NoSpSuIce and leads to a larger net effect on ozone. At middle latitudes the annual average changes are much smaller but they broadly follow the changes found at polar latitudes. In run NoAugSepIce (only late-summer perturbation), the changes in the Arctic/midlatitude annual ozone burdens relative to Base (not shown) are close to zero, even though there are detectable changes (4−5%) in Arctic $P(O_3)$ and $L(O_3)$. This indicates that a possible late-summer full sea-ice retreat is not expected to have any impact on the annual ozone burden via photolysis.

5. Conclusions

[16] It is clear that the removal of Arctic sea-ice has the potential to alter oxidant concentrations drastically in the future. The effects could be very large directly over the Arctic, with up to around 60% reductions in August surface OH and 50% increases in early spring surface ozone. Substantial changes in summer OH could occur soon, since they are associated with sea-ice disappearance in late summer, which is projected by studies for later in this century [e.g., *Holland et al.*, 2006; *Wang and Overland*, 2009]. The changes in ozone reflect a more extreme scenario of sea-ice reduction. If year-round sea-ice is impacted by climate change, then reductions in spring will impact the release of bromine, with a consequent effect on ozone. Our calculations suggest that the impact of the sea-ice retreat on significantly populated boreal regions could be an increase in surface ozone concentrations of up to about 20%.

[17] We have not taken into account the potential changes in atmospheric humidity caused by the sea-ice removal, which should be a focus of a future study. Also, we have looked at the effect of a complete summer and spring sea-ice removal on oxidants. A different scenario is one in which summer sea-ice retreats completely, but where we have young sea-ice covering the Arctic in the winter and

early spring. Young sea-ice is more saline and more effective in bromine release than multiyear sea-ice, so in that case, we could expect more ozone depletion and thus less spring surface ozone at high latitudes in the future. This intermediate case should also be examined in future work. Nevertheless, our work suggests that future sea-ice reduction could lead to possibly important changes in oxidation over the Arctic in the future, which could even have implications for regions outside of the Arctic, under specific conditions. This can be a critical issue, since the northern high-latitude regions not only include very important ecosystems, but they also could face a substantial increase of human population in a changing world with a warming climate. A shift of the northern high-latitude chemical regime from ozone destroying to ozone producing due to more NO_x emissions and changes in transport patterns, can only complicate the issue further. Thus, future research needs to consider all the factors involved, including the albedo and bromine effects analyzed here, in order to contribute to a more solid understanding of Arctic oxidation chemistry.

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